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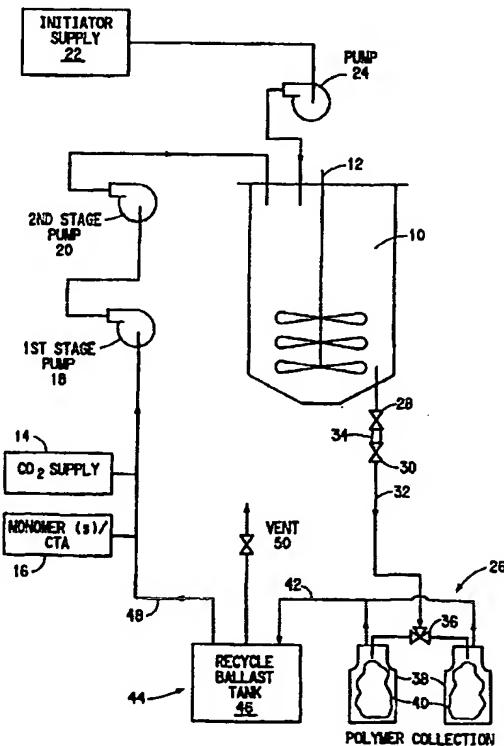
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(54) Title: POLYMERIZATION OF FLUOROMONOMERS IN CARBON DIOXIDE

(57) Abstract

Fluoromonomer is polymerized to obtain a fluoropolymer with the polymerization being carried out in a pressurized polymerization reactor containing a polymerization medium comprising liquid or supercritical CO<sub>2</sub>. The polymerization medium is withdrawn from the reactor together with the fluoropolymer and flash decompressed to thereby recover the fluoropolymer from the medium.



**TITLE**

POLYMERIZATION OF FLUOROMONOMERS IN CARBON DIOXIDE

**FIELD OF THE INVENTION**

The present invention relates to polymerization of fluorinated  
5 homopolymers and copolymers in a pressurized reactor containing a  
nonaqueous medium comprising liquid or supercritical carbon dioxide.

**BACKGROUND OF THE INVENTION**

Various methods for the polymerization of fluoropolymers in a  
nonaqueous medium of comprising liquid or supercritical carbon dioxide  
10 have been proposed. U.S. Patent No. 5,496,901 discloses a processes for  
the making a variety of fluoropolymers comprising solubilizing a  
fluoromonomer in a solvent comprising carbon dioxide. PCT Publication  
No. WO 96/28477 discloses polymerization of a variety of fluoropolymers  
in a solvent comprising carbon dioxide while employing an initiator capable  
15 of producing stable end groups. These publications describe processes  
which work in laboratory scale reactors, e.g., 25-500 ml, when run in a  
batchwise fashion. In the Examples of these publications, the  
polymerization is run and then the reactor is vented and opened to recover  
the product. Such processes are not applicable to the commercial  
20 production of fluoropolymers where it is desired to recover product without  
having to disassemble the reactor.

Japanese Patent Publication Kokai 6(1994)345824 discloses  
polymerizing TFE with fluorine-containing vinyl ethers in liquid carbon  
dioxide. A chemical initiator is used. Japanese Patent Publication Kokoku  
25 45(1970)3390 discloses the polymerization of either TFE or a TFE/olefin  
(hydrocarbon) copolymer in liquid carbon dioxide using irradiation with  
gamma rays to cause the polymerization. Continuous processes are  
mentioned in these references but only laboratory scale batch processes are  
illustrated in the examples.

**SUMMARY OF THE INVENTION**

In a process in accordance with the invention, fluoromonomer is  
polymerized to obtain a fluoropolymer with the polymerization being  
carried out in a pressurized polymerization reactor containing a  
polymerization medium comprising liquid or supercritical CO<sub>2</sub>. The  
35 process further includes withdrawing the polymerization medium from the  
reactor together with the fluoropolymer and flash decompressing the  
withdrawn polymerization medium to thereby recover the fluoropolymer  
from the medium.

fluoromonomers, or may be copolymers of at least one fluoromonomer and at least one fluorine-free monomer.

"Fluoromonomers" is used in this application to mean compounds containing a vinyl group that may be free-radically polymerized and that contain at least one fluorine atom, fluoroalkyl group, or fluoroalkoxy group attached to the vinyl group that undergoes polymerization. Useful fluoromonomers include, but are not limited to, vinyl fluoride; vinylidene fluoride; trifluoroethylene; chlorotrifluoroethylene (CTFE); 1,2-difluoroethylene; tetrafluoroethylene (TFE); hexafluoropropylene (HFP); perfluoro(alkyl vinyl) ethers such as perfluoro(methyl vinyl) ether (PMVE), perfluoro(ethyl vinyl) ether (PEVE), and perfluoro(propyl vinyl) ether (PPVE); perfluoro(1,3-dioxole); perfluoro(2,2-dimethyl-1,3-dioxole) (PDD);  $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{X}$  wherein X is  $\text{SO}_2\text{F}$ ,  $\text{CO}_2\text{H}$ ,  $\text{CH}_2\text{OH}$ ,  $\text{CH}_2\text{OCN}$  or  $\text{CH}_2\text{OPO}_3\text{H}$ ;  $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{SO}_2\text{F}$ ;  $\text{F}(\text{CF}_2)_n\text{CH}_2\text{OCF}=\text{CF}_2$  wherein n is 1, 2, 3, 4 or 5;  $\text{R}^1\text{CH}_2\text{OCF}=\text{CF}_2$  wherein  $\text{R}^1$  is hydrogen or  $\text{F}(\text{CF}_2)_m$ - and m is 1, 2 or 3; and  $\text{R}^3\text{OCF}=\text{CH}_2$  wherein  $\text{R}^3$  is  $\text{F}(\text{CF}_2)_z$ - and z is 1, 2, 3 or 4; perfluorobutyl ethylene (PFBE); 3,3,3-trifluoropropene and 2-trifluoromethyl-3,3,3-trifluoro-1-propene. Preferred fluoromonomers are 3,3,3-trifluoropropene, 2-trifluoromethyl-3,3,3-trifluoro-1-propene, PFBE, vinyl fluoride, vinylidene fluoride, TFE, HFP, PMVE, PEVE, PPVE, CTFE, and PDD.

The fluoromonomer may be polymerized alone to form a homopolymer if the fluoromonomer can be homopolymerized, or may be polymerized with one or more other fluoromonomers or other monomers that are not fluoromonomers to form a copolymer. If a copolymer is to be formed, the monomers chosen must be able to copolymerize. Fluorine-free monomers that copolymerize with some combinations of fluoromonomers include propylene and ethylene. Examples of useful homopolymer fluoropolymers include polytetrafluoroethylene (PTFE). Also usually classed with homopolymer PTFE are the modified PTFE polymers containing fluoromonomers other than TFE in such minor amounts that the modified polymers retain the non-melt-fabricable character of PTFE. Examples of useful copolymers include the copolymers of TFE with HFP and/or perfluorinated vinyl ethers such as PPVE or PEVE, copolymers of TFE with PMVE, copolymers of TFE with PDD, and copolymers of TFE or CTFE with ethylene. Further examples include the copolymers of vinylidene fluoride with HFP, or with HFP and TFE. As implied above,

The CO<sub>2</sub> and monomer are fed to first and second stage pumps, 18 and 20 which are used to increase the pressure of the CO<sub>2</sub> and monomers and feed them to the reactor. The first stage pump pumps the gases to a pressure of about 0.35 to about 1 mPa. The second stage pump pumps the gases to a pressure of about 7 to about 10 mPa. If desirable, a third stage pump can be used to reach pressures up to about 140 mPa. Preferably, when potentially explosive fluoromonomers such as TFE are used, the monomers are mixed with adequate amounts of CO<sub>2</sub> to prevent the mixtures from being explosive under the conditions present during pumping and in the reactor 10.

An initiator supply 22 is used to supply a metered amount of initiator to a initiator pump 24 so that they can be supplied into the reactor 10. Suitable initiators include any of variety of known initiators which initiate free radical polymerization and, since they typically provide the end group for the polymer chain, the initiator also can provide stable end groups to the polymer if desired. Preferably, the initiator is halogenated and most preferably is fluorinated. As will be discussed in more detail hereinafter, it also preferable for the initiator to be collected with the product under the conditions present in the recycle system. For example, a particularly desirable initiator is hexafluoropropylene oxide (HFPO) dimer peroxide  $[(CF_3CF_2CF_2OCF(CF_3)COO)_2]$ .

Temperature and pressure conditions in the reactor are selected to maintain the CO<sub>2</sub> in the medium in the desired form, i.e., liquid or supercritical, to control the reaction rate, and to adjust product properties and yield. Typically, the temperature is kept between about 10 and about 80°C. Pressures are typically between 6.2 mPa and 10.3 mPa. Residence times are highly dependent upon the specific process being run in the reactor but typically range from about 10 to about 120 minutes.

A process in accordance with the invention further includes withdrawing the polymerization medium from the reactor together with the fluoropolymer and flash decompressing the withdrawn polymerization medium to thereby recover the fluoropolymer from the medium. This is advantageously accomplished using a polymer recovery system 26 of the type illustrated in Figure 1. Preferably, this system successively withdraws and isolates portions of the polymerization medium including the fluoropolymer from the reactor and the flash decompression is carried out on each of these portions. The preferred recovery system 26 depicted includes upper and lower ball valves, 28 and 30 respectively, in the effluent

The rapidly flowing gases and entrained polymer pass through a three-way valve 36 which is open to one of two collection vessels 38. The three-way valve 36 facilitates the changing of collection vessels since the gas and entrained polymer particles is directed into only one vessel a time.

- 5 Inside each collection vessel 38 is a filter bag 40 of a suitable woven or nonwoven fabric which catches the polymer but which permits the gases to pass through. Gases exit each of the collection bottles through line 42 for recycling by a recycling system 44.

- Recycling system 44 includes the capability to reuse the reusable  
10 components of the gas stream, i.e., CO<sub>2</sub> and unreacted monomers. The recycling system 44 includes a monomer/CO<sub>2</sub> ballast tank 46 which reduces the pressure variation and homogenizes the composition of the recycle stream and a return line 48 which provides the recycle gas stream to the line feeding the first stage pump 18. The ballast tank 46 includes a low volume  
15 vent 50 which performs two major functions. The vent is needed to remove excess CO<sub>2</sub> to enable the use of a feed mixture of TFE and CO<sub>2</sub> which, in the event the recycle gases are cut off or reduced, can be safely compressed to reactor pressures. In addition, the vent 50 prevents build-up of impurities and by-products in the recycle gas stream. If desired, the impurities and by-  
20 products can be removed from this vent stream and CO<sub>2</sub> and monomers can be recycled for use in the process.

- The control of the process is preferably performed by a microprocessor (not shown). The inputs to the microprocessor preferably include measurements from a gas chromatograph which monitors the  
25 composition of the gases in the recycle composition and the monomer supply streams. Flow rates of the vent 50 and monomer supply are also input. Pressure and temperature of the reactor are also measured. Based on the inputs, the microprocessor controls the sequencer operating the ball valves 28 and 30, supply flows and vent flow.

- 30 While the process of the invention can be used for batch and semi-continuous operation, the invention is advantageously used in processes in which the polymerizing is carried out continuously by continuously feeding CO<sub>2</sub> and fluoromonomer into the reactor and continuously withdrawing the contents of the reactor, including unreacted  
35 fluoromonomer, the CO<sub>2</sub>, and the fluoropolymer. It is further preferred to feed CO<sub>2</sub> and fluoromonomer and to withdraw the contents of the reactor in such a manner that a substantially steady state composition of the medium

<b>Table 2</b>			
	<b>Sample 1</b>	<b>Sample 2</b>	<b>Sample 3</b>
	<b>8-10 hr</b>	<b>12-14 hr</b>	<b>16-20 hr</b>
DSC 1st Heat (°C)	304	303	303
Viscosity (10 <sup>4</sup> Poise)	3.39	3.39	2.82
NMR Analysis (wt%)			
TFE	96.40	96.33	96.19
PEVE	3.58	3.66	3.80
Polymer Produced (g)	60.6	65.0	124.7

**Example 2**

This example illustrates the polymerization of TFE/HFP/PEVE terpolymer in a continuous reaction.

- 5       The procedure of Example 1 is used except that HFP is also used and that the conditions and monomer feeds are as indicated in Table 3. Product samples are taken periodically and the results reported in Table 4. The average space time yield of this continuous process is 0.3 lb/gal·hr (35.5 g/L·hr).

10

<b>Table 3</b>	
Reactor Temperature	25°C
Reactor Pressure	1050 psig (7.34 mPa)
Agitator Speed	600 rpm
CO <sub>2</sub> Feed Rate	260 g/hr
TFE Feed Rate	55 g/hr
HFP Feed Rate	200 g/hr
PEVE Feed Rate	4.0 g/hr
Initiator Feed Rate	0.018 g/hr

<b>Table 4</b>			
	<b>Sample 1</b>	<b>Sample 2</b>	<b>Sample 3</b>
	<b>4-6 hr</b>	<b>8-10 hr</b>	<b>12-14 hr</b>
DSC 1st Heat (°C)	291	289	287
Viscosity (10 <sup>3</sup> Poise)	3.78	5.19	-
Polymer Produced (g)	69.6	71.8	71.5

results reported in Table 8. The average space time yield of this continuous process is 1.23 lb/gal·hr (148 g/L·hr).

**Table 7**

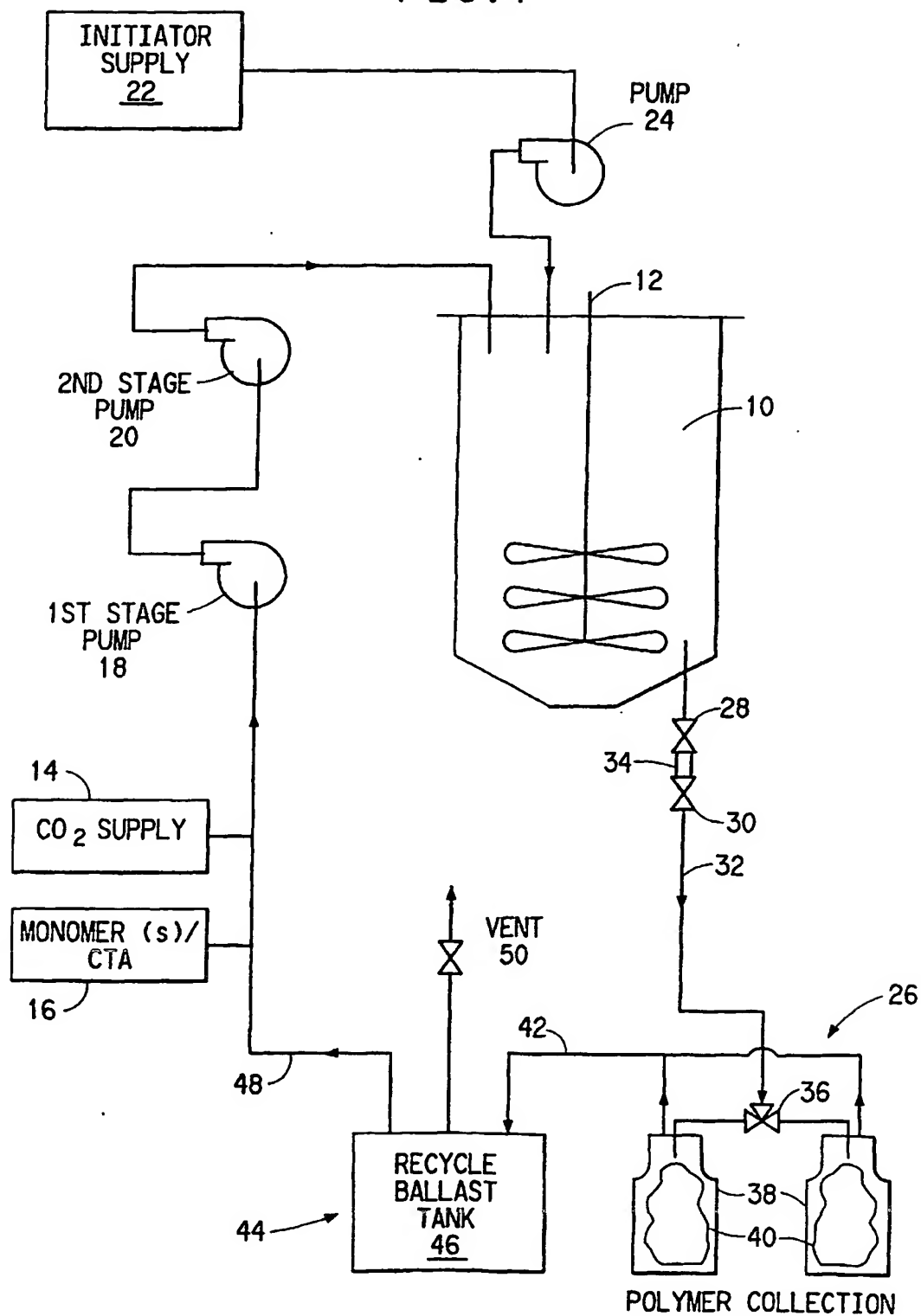
Reactor Temperature	40°C
Reactor Pressure	2000 psig (13.9 mPa)
Agitator Speed	800 rpm
CO <sub>2</sub> Feed Rate	300 g/hr
TFE Feed Rate	230 g/hr
PEVE Feed Rate	70 g/hr
Ethane Feed Rate	0.4 g/hr
Initiator Feed Rate	0.18 g/hr

**Table 8**

	Sample 6	Sample 7	Sample 8
	17-19 hr	20-22 hr	23-25 hr
DCS 1 <sup>st</sup> melt (°C)	288	288	289
2 <sup>nd</sup> melt (°C)	280	279	281
Viscosity (10 <sup>4</sup> Poise)	2.78	2.77	2.90
FTIR Analysis (wt%)			
TFE	94.10	94.04	94.24
PEVE	5.90	5.96	5.76
Polymer Produced (g)	449	454	469

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FIG. 1





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